

AMENDMENTS TO THE SPECIFICATION

1. Please amend the abstract as follows:

“~~A method~~ A method for removing hydrogen sulphide and carbon dioxide from a gas stream includes the step of contacting the gas stream with aqueous and gaseous ammonia in a closed vessel in the presence of solid iron. An apparatus for removing hydrogen sulphide and carbon dioxide from a gas stream includes a closed vessel for containing aqueous and gaseous ammonia and an iron source. The vessel is partitioned into inlet and outlet chambers and may itself serve as the iron source.”

2. Please amend the specification as follows:

[0004] Produced natural gas at the wellhead often contains hydrogen sulphide. Small amounts of hydrogen sulphide are routinely removed from produced gas before distribution to customers by passing it through heated amine scrubbers at a significant capital and operating cost. Large amounts of hydrogen sulphide and other undesirable gases in produced ~~gas~~ are much more expensive to remove. Often gas wells with high H₂S and/or CO₂ to hydrocarbon gas ratios are left dormant because of the high cost of H₂S and/or CO₂ removal.

[0007] It is also known to remove hydrogen sulphide from gases by contacting them with iron oxide in the form of pellets, powder or iron oxide sponge. { Iron sulphide is formed which is then reacted with oxygen to regenerate the iron oxide and form elemental sulfur. This process does not affect or remove other acid gases such as carbon dioxide. Also, the removal of spent iron oxide sponge impregnated with sulfur is a difficult and noxious task.

[0008] Therefore, there is a need in the art for a method and apparatus for efficiently removing acid gases including H₂S and CO₂, which does not involve incineration and is cost-effective. Simultaneous removal of H₂S and CO₂ is particularly desirable due to CO₂ being a serious pollutant, and a flame retardant in any combustion process. It

would be advantageous if the apparatus were compact and portable allowing installation and practice of the method ~~on~~ on a relatively small scale. Such a method and apparatus may permit the reclamation of low volume gas wells previously deemed uneconomic.

[0009] We have found that acid gas removal may be efficiently and effectively accomplished by contacting a gas stream comprising the acid gas or gases with gaseous and aqueous ammonia in the presence of solid iron, preferably but not necessarily at substantially standard pressure and ambient temperature. The presence of solid iron appears to have surprising and unexpected beneficial effects on the ability of the ammonia to react with the acid gas or gases and to remove it from the gas stream.

[0013] (c) providing a source of solid iron in contact with either or both of the gas and liquid phases;

[0016] Where the acid gas comprises hydrogen sulphide, it is believed that the overall reactions taking place in this process are as follows: N

[0018] $\text{NH}_3 \text{ (g)} + \text{H}_2\text{S} \text{ (g)} \rightleftharpoons \text{NH}_4\text{HS} \text{ (aq)}$ (dissociates to ammonium ions and bisulphide ions into solution) (1)

[0042] In its method form, the invention comprises the treatment of a gas stream to remove acid gases by contacting the gas stream with gaseous and aqueous ammonia in the presence of solid iron. The present invention has primary application to the removal of hydrogen sulphide and carbon dioxide from a gas stream emanating from produced or stored unrefined crude petroleum oil. The present invention may also be adapted to treat sour natural gas at the wellhead or any other source of ~~a n~~ desirable of undesirable acid gases, which may include from air or gaseous clean-out operations performed within existing wells where foam and/or liquids may be used as viscosifying carrying agents, from under-balanced air or gaseous drilling of a well where foam

and/or liquids may be used as viscosifying carrying agents, from drill stem testing or production testing or from any other waste gas streams such as well workovers, well recompletions, well completions, well pressure transient surveys, flowline/pipeline decompressions and evacuations, oil and gas plant maintenance turn-arounds, casing gas venting, truck venting or automotive exhaust gas emissions.

[0043] In one embodiment, the acid gases in the present invention are removed by contact with gaseous ammonia in the presence of iron, under low or moderate pressure, at ambient temperatures in a closed system. The system is closed to atmospheric oxygen and nitrogen ~~and except~~, except for any nitrogen and oxygen which may be part of the gas stream being treated. The iron may be provided in the form of carbon steel and preferably low carbon steel where the carbon and chromium content each do not exceed about 0.07%. Those skilled in the art may readily adapt the present invention to treat high-pressure gas streams by utilizing pressure rated vessels and appropriate inlet and outlet fittings. Such adaptations are intended to be included within the scope of the invention claimed.

[0044] Without being limited to a theory, it is ~~believed~~ believed that the ammonia, evolved from aqueous ammonia solution, and hydrogen sulphide react, in the presence of solid iron to form ammonium ~~sulfiphe~~ bisulphide (ammonium hydrogen sulfiphe sulphide). The ammonium bisulphide is very soluble in water and therefore will dissolve and immediately dissociate into ammonium and bisulphide ions. Bisulphide ions do not dissociate readily into hydrogen ions and sulphide ions, but some bisulphide ions will react with iron to form iron II ions, likely by the action of the hydrogen in the bisulphide ions on the iron, i.e., making iron more positive by removing two electrons from each iron atom. This leaves sulphide ions and iron II ions in proximity of each other. Since iron II ~~sulfiphe~~ sulphide is insoluble in water, iron II ~~sulfiphe~~ sulphide precipitates. Hydrogen gas will be a by-product of this reaction.

[0045] Another perspective is that the hydrogen ~~sulfiphe~~sulphide gas reacts with the ammonia gas, in the presence of water vapour and iron in low carbon steel, to produce hydrated ammonium ions and hydrated bisulphide ions. Even though many steps are likely involved in these reactions, in the system, the reactions described may be good approximations of overall processes. The actual mechanism or mechanisms of the reactions occurring in the ~~system~~epend system, depend on the ambient temperature, moisture, pH of the solution, and gas concentrations in the reactor, at a particular point in time. The claimed invention is not intended to be limited by any specific reactions or mechanisms described or suggested herein.

[0046] It is also believed, without being limited to a theory, that the carbon dioxide in the gas stream also reacts with ammonia, but more slowly than does the hydrogen ~~sulfiphe~~sulphide, to form mostly ammonium bicarbonate. This reaction likely takes place in the gas phase but is assisted by the presence of solid iron. Since iron is a crystalline substance, unlike pipe coatings or plastic pipes such as Teflon™ coating or ABS plastic, the ammonium bicarbonate uses the iron only as a crystallisation site. Ammonium bicarbonate is also soluble in most aqueous solutions.

[0047] In one embodiment, the above-described processes take place in a closed vessel, at substantially atmospheric pressure and at ambient temperature. In a typical application, the pressure may be slightly elevated as a result of the incoming gas stream pressure but only slightly so. Therefore, it is not necessary for the vessel to be pressure-rated. However, the present invention is not limited to atmospheric or low pressure applications. The chemical reactions appear to be primarily exothermic so that the process temperature may also be slightly ~~elevated~~elevated. It is believed that internal vessel temperatures do not exceed 50° C during operation.

[0048] In its apparatus form, one embodiment of the invention is represented in Figure 2 as a closed reactor vessel (10). The vessel is made from low carbon steel and may

preferably be formed, but not necessarily, as a horizontally cylindrical vessel having end walls(11). walls (11). In one embodiment, the vessel is partitioned internally by a single reverse weir (12) to create an inlet chamber (14) and a downstream outlet chamber (16). The reverse weir (12) leaves a small opening at the bottom permitting fluid communication between the inlet and outlet chambers. Preferably, the inlet chamber is smaller than the outlet chamber and more preferably is about one-half the size of the outlet chamber.

[0052] A gas inlet (22) with a ball valve (23) is provided at the top of the inlet chamber (14). In one embodiment, the gas inlet is a coupling (22), which connects to the gas stream source. A gas outlet (24) is provided at the top of the outlet chamber. In one embodiment, the gas outlet includes a baffle tower (26) in which residual gas scrubbing takes place, predominantly of carbon dioxide if it is present in the gas stream. The baffle tower (26) comprises of a substantially vertical tower (28) having a plurality of internal baffles (30), which interrupt and divert the gas flow as it passes through the tower (28). In a preferred embodiment, the tower (28) comprises an elongated square insert having a length to width ratio ratio of about 3.5:1. The top of the tower (28) is sealed except for a coupling (32) for the gas exit. There are a plurality of baffles (30), each of which transverses the tower (28), preferably angled downward at about 30°. The baffles alternate from each side of the tower as is illustrated in Figure 2. As will be appreciated, the gas phase undergoes significant turbulence, and therefore mixing, as it passes through the baffle tower (26). Preferably, the baffles (30) and tower (28) are made from the same low carbon steel as the vessel and are uncoated. It is believed that the iron in the low carbon steel facilitates the reaction of carbon dioxide and ammonia, evidenced by the deposition of ammonium bicarbonate on the baffles during operation.

[0053] In one embodiment, the baffle tower (26) may be hinged (31) to open up to facilitate cleaning the baffle tower (26).†

[0054] In another embodiment, a vessel (410) having a reverse weir (412) is shown in Figure 4. In this embodiment, the baffles [insert rest of para 54]

[0055] In one embodiment, a liquid phase re-circulation system is used to increase the concentration of ammonia in the gas phase thereby increasing the exposure of the acid gases to ammonia. The re-circulation system may also function to wash any solids which form on the inner surface of the vessel (10) into the liquid phase. The re-circulation system includes a small pump (34) which draws fluid from the bottom of the vessel and pumps it through a spray bar (36) having a plurality of perforations acting as nozzles. The spray bar (36) is situated near the top of the vessel and sprays the liquid through the gas phase and onto the inner surface of the vessel. Alternatively or in addition to the spray bar (36), the pump may occasionally pump liquid to the top of the baffle tower (28) where it is sprayed onto the baffles and allowed to trickle down through the baffle tower. Power for the pump may be supplied from any electrical source, air source, natural gas source or photovoltaic cells (not shown) if power lines are not available at the installation site.

[0058] In one embodiment, the vessel (10) is made from 36,000-psi 00ew low carbon steel and is horizontally cylindrical. The vessel may be approximately 38 inches in diameter and 45 inches long. As such, the internal volume is approximately 29 cubic feet or 817 liters. The reverse weir (12) transversely divides the vessel (10) into inlet and outlet chambers where the outlet chamber (16) is approximately twice the size of the inlet chamber (14). It is to be understood that the dimensions or orientation of the vessel and the chambers are not limitations of the claimed invention unless specifically claimed to be so. The size of the vessel may be tailored to the expected gas volume and flow rate of the particular source of gas stream to be treated.

[0060] In another embodiment employing a vessel of larger capacity, as seen in Figure 3, the vessel (310) is horizontally cylindrical, approximately 72 inches long and approximately 38 inches in

diameter. The vessel is internally divided into four chambers by three weirs. The first weir (312) extends upwardly to separate the gas inlet chamber (314) (314) leaving a gap at the top of the vessel. The gas inlet chamber includes a quantity of ammonia solution as do the downstream chambers. The gas inlet includes a downcomer (316) to bubble the incoming gas through the liquid phase in the gas inlet chamber (314). The second (318) and third (320) weirs are reverse weirs. In this embodiment, the incoming gas accumulates in the gas inlet chamber (314) and the second chamber (319) until the liquid level in the second chamber falls below the level of the second weir (318). A quantity of gas then transfers to the third chamber (321). When sufficient gas has accumulated in the third chamber (321) to drive the liquid level below the level of the third weir (320), a quantity of gas then transfers to the fourth (gas outlet) chamber (322). Preferably, the gap underneath the third weir (320) is higher than the gap left by the second weir (318) in order to prevent reverse transfer of gas within the vessel (310).

[0064] In use, the vessel (10) is partially filled with a concentrated ammonia solution to a level which at least covers the gap of the reverse weir (12), or the highest reverse weir, if there are more than one. The ammonia solution preferably has a concentration of ammonia of about 25 grams per 100 ml of solution or ~~26 BE~~, 26 BE. Preferably, the vessel is filled with the ammonia solution between about 2 % to about 20 % of its volume. More preferably, the vessel is filled to about 5 % to about 15 % of its volume with the ammonia solution. Because of the significant vapor pressure of ammonia, which largely remains unreacted and in molecular form in water, much as carbon dioxide does in water, any rise in temperature will accelerate the effervescence of ~~ammonia~~ ammonia, and cause a significant portion of the ammonia to effervesce over time and occupy the vessel as the ~~gas phase~~ phase. This movement of ammonia to the gas phase is a natural tendency (it is an entropy increase) and is possible through a wide range of temperatures.

[0066] In one embodiment, the liquid phase may also comprise a surfactant to control the evaporation rate of the ammonia from the liquid phase. The surfactant will cause a foam layer to float on the liquid phase, thereby limiting ammonia evaporation from the

liquid phase. Suitable surfactants include nonionic, anionic or cationic surface tension reducing agents[~~such~~ agents such] as fatty acid soaps. Preferred surfactants are ones that increase in viscosity as their temperature rises. Silicon based surfactants which increase in viscosity with a concomitant rise in surface tension as the temperature rises, may assist to prevent the release of excess gaseous ammonia within the vessel.

[0070] The liquid phase may be withdrawn at regular intervals along with any ~~precipitated~~ precipitated solids such as iron sulphide, and dissolved ammonium bicarbonate, ~~an~~ solved bicarbonate, dissolved ammonium bisulphide, and dissolved ammonium sulphide and replaced with a fresh charge of aqueous ammonia, which may include a surfactant and a strong base as described above.

[0077] A horizontally cylindrical vessel formed of 36,000 psi uncoated low carbon steel was provided, substantially as illustrated in Figure 2. A 60 litre charge of ~~an~~ a 26 BE ammonia solution including 0.2 % surfactant and 1.75 % potassium hydroxide (v:v concentrated KOH) was connected to the gas effluent from a crude oil storage tank. The incoming gas pressure was approximately 1 to 3 ounces above atmospheric pressure. A small pump powered by natural gas was used to re-circulate the liquid phase through both a spray bar and to the top of the baffle tower as described above. The incoming gas was tested using a laboratory gas chromatograph showing the gas concentrations shown in Table 1 below. The effluent from the gas outlet was tested both with a field GasTee Gas Tec™ unit and with a laboratory gas chromatograph. As is apparent, the hydrogen sulphide concentration was reduced to a negligible level and carbon dioxide reduced to undetectable level.

[0079] [+1]

[TABLE 1]

Gases	Chromatographic Gas Concentration <u>Concentration</u> Before REACTOR (PPM)	Gas Tec™ Gas Concentration After Scrubbing (PPM)	Chromatographic Gas Concentrations; Output from REACTOR (PPM)
Hydrogen Sulphide	148,400	28	0.0
Carbon Dioxide	266,300	0	0.0
Hydrogen	700	N/A	3000

A black precipitated solid was found in the bottom of the vessel and determined to be iron sulphide. Also, ammonium bicarbonate was found within the vessel and encrusted to the baffles in the baffle tower indicating that the ammonia – carbon dioxide reaction took place in the baffle tower. After desiccation, the liquid phase was found to include ammonium bisulphide, ammonium sulphide, iron II sulphide, and ammonium bicarbonate, all in solid crystalline form.

[0082] [+2]

TABLE 2

GASES	Chromatographic Gas Concentration Before REACTOR (PPM)	GasTec™ Gas Concentration After Scrubbing(PPM)	Chromatographic Gas Concentrations; Output from REACTOR (PPM)
Hydrogen Sulphide	110,100	0	0
Carbon Dioxide	121,300	0	0
Hydrogen	0	n/a	4,400

[0083] After desiccation of the liquid phase, it was was found to include ammonium bisulphide, ammonium sulphide, iron II sulphide, and ammonium bicarbonate, all in solid crystalline form.